

In the specification:

Page 1, line 1, cancel --Description--.

Page 1, just above line 6, insert the heading "Field of the Invention".

Page 1, just above line 13, insert the heading "Background".

Page 4, just above line 19, insert the heading "Summary of the Invention".

Page 4, line 28, cancel from the period through end of the paragraph on Page 5, line 7.

Page 5, line 9, cancel --possible-- and insert "possibly".

Page 6, cancel from line 16 through Page 10, line 20.

Page 10, just above line 22, insert the heading "Brief Description of the Drawings".

Page 10, just above line 29, insert the heading "Description of the Preferred Embodiment".

Page 10, just below the heading "Description of the Preferred Embodiment" insert:

The invention is based on the finding that currently used ceramic thermal barrier coatings, despite the use of, e.g., partially stabilized zirconium oxide, have a thermal expansion coefficient which at maximum is only about 70% of the thermal expansion coefficient of the metallic basic body used, particularly of a superalloy. This lower thermal expansion coefficient of the zirconium oxide thermal barrier coatings compared to the metallic basic body causes thermal stresses during exposure to a hot gas. To counteract such resultant stresses occurring under alternating thermal stress, an expansion-tolerant microstructure of the thermal barrier coating is required, e.g., by adjusting a corresponding porosity or a columnar structure of the thermal barrier coating. In a zirconium oxide-based thermal barrier coating, continuous sintering of the coating material furthermore takes place during operation [missing verb] a change in the microstructure, disappearance of the porosity, occurrence of new defects or cracks, and possible failure of the thermal barrier coating in thermal and mechanical respects. In addition, in a thermal barrier coating of partially stabilized zirconium oxide by means of stabilizers such as yttrium oxide, cerium oxide or lanthanum oxide, stresses may occur that are created due to a thermally associated phase transition (tetragonal to monoclinic and cubic). Due to the associated volume change, a maximum permissible surface temperature for thermal barrier coatings made of zirconium oxide is given.

The use of a spinel provides a thermal barrier coating, possible taking into account mixed crystal formation and microstructure modification, with a high thermal expansion coefficient, low thermal conductivity, a high melting point, high chemical stability, a reduced tendency toward sintering, and a high phase stability.

According to the invention, the product-related object is attained in that the thermal barrier coating has a spinel of the composition  $AB_2X_4$ , where

X represents oxygen, sulfur, selenium and/or tellurium. A represents an element or several elements of the group comprising aluminum, magnesium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, silicon, titanium and tungsten. B represents one or several elements of the group comprising aluminum, magnesium, manganese, iron, vanadium, chromium, gallium, silicon, titanium, sodium and potassium.

The thermal barrier coating is bonded to the basic body either directly or indirectly via a bond coat. Bonding is preferably effected via an oxide layer that is formed, for example, by oxidation of the basic body or of the bond coat. Bonding can also or additionally be effected through mechanical anchoring, e.g., through roughness of the basic body or the bond coat.

Such a thermal barrier coating particularly serves to prolong the life of products that are subjected to a hot gas, e.g. gas turbine components, blades and heat shields. It exhibits low thermal conductivity, a high melting point, and is chemically inert.

It should be noted that the compound  $MgAl_2O_4$  (magnesium aluminate) is already frequently termed the spinel. The term spinel, as used in the invention, signifies the aforementioned group of compounds of the general formula  $AB_2X_4$ . The term "spinel" is intended to mean the so-called normal spinels ( $AB_2X_4$ ) as well as the "inverse" spinels ( $B(AB)_2X_4$ ). In addition to the conventional spinels, in which X represents oxygen, material systems where X represents selenium, tellurium or sulfur are also included. In the normal spinel type, the oxygen atoms form a nearly cubic-dense lattice, in the tetrahedral vacancies of which there are 8 A atoms and in the octahedral vacancies of which there are 16 B atoms. In contrast, in what is known as an inverse spinel, 8 B atoms are present in tetrahedral and the remaining 8 B atoms and the 8 A atoms in octahedral coordination.

Preferably, the product has a spinel with oxygen. Here, A represents a metallic element of valence  $2^+$  and B a metallic element of valence  $3^+$  (so-called 2-3 spinels). In this class of spinels, A represents preferably magnesium, iron, zinc, manganese, cobalt, nickel, titanium, copper or cadmium, and B represents aluminum, iron, chromium or vanadium.

Preferably, the spinel has aluminum or chromium as the B element and magnesium, nickel, or cobalt as the A element.

Furthermore, the thermal barrier coating preferably has a spinel in which B represents magnesium and A titanium.

In addition to the aforementioned 2-3 spinels with the valence  $A^{2+}$  and  $B^{3+}$ , there are other spinel types with a different valence of the cations, e.g., 1-6 spinels ( $WNa_2O_4$ ) and 2-4 spinels (e.g.  $Fe_2TiO_4$ ). In addition to the aforementioned elements that can represent the symbol A, aluminum, silicon, titanium and tungsten may also be used. B also comprises the elements magnesium, manganese, gallium, silicon, sodium and potassium.

The thermal conductivity of a preferred spinel is between 1.0 W/mK and 5.0 W/mK. The thermal expansion coefficient is preferably between  $6 \times 10^{-6} K$  and  $12 \times 10^{-6} K$  and the melting point is greater than  $1600^\circ C$ . The

indicated ranges for expansion coefficient and thermal conductivity apply to bodies of a ternary oxide with and "ideal" cell structure in manufacturing terms, i.e., without specifically introduced porosities. For  $\text{MgAl}_2\text{O}_4$ , e.g., the melting point is approximately  $2100^\circ\text{C}$ , thermal conductivity is  $4.0\text{ W/mK}$  at  $1945^\circ\text{C}$  and the thermal expansion coefficient is  $7.6$  to  $9.2 \times 10^{-6}/\text{K}$  at temperatures between  $25^\circ$  and  $1200^\circ\text{C}$ . For  $\text{CoAl}_2\text{O}_4$  the melting point is approximately  $1955^\circ\text{C}$  and the thermal expansion coefficient is between  $7$  and  $11 \times 10^{-6}/\text{K}$  at temperatures of between  $500^\circ$  and  $1500^\circ\text{C}$ . For  $\text{MgCr}_2\text{O}_4$  a melting point on the order of magnitude of  $2400^\circ\text{C}$  applies, a thermal expansion coefficient of between  $6.5$  and  $7.6 \times 10^{-6}/\text{K}$  at  $25^\circ$  to  $1200^\circ\text{C}$ , and a thermal conductivity [ $\text{W/mK}$ ] of  $1.4$  in the range of  $25^\circ$  to  $300^\circ\text{C}$ . For  $\text{CoCr}_2\text{O}_4$  the melting point is above  $1600^\circ\text{C}$  and the thermal expansion coefficient is between  $7.5$  and  $8.5 \times 10^{-6}/\text{K}$  at  $500^\circ$  to  $1500^\circ\text{C}$ . The compound  $\text{TiMg}_2\text{O}_4$  has a melting point of  $1835^\circ\text{C}$  and a thermal expansion coefficient of  $6$  to  $12 \times 10^{-6}/\text{K}$  in the range of  $500^\circ$  to  $1500^\circ\text{C}$ .

Preferably, the spinel is present as a mixture in the ternary system of the type  $\text{AB}_2\text{X}_4\text{-AX-B}_2\text{X}_3$ . A metallic mixed oxide system with the spinel and an additional compound, particularly an oxide, may also be present. The spinel, or the spinel present as a mixture, can have an oxide or several oxides of the group comprising  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$ . This can be the case even if said oxides are not already a component of the spinel. In particular, said oxides can be present in an aluminate or a chromate spinel.

Furthermore, the spinel or a spinel consisting of a mixture can have an oxide or several oxides of the group comprising magnesium oxide ( $\text{MgO}$ ), zirconium oxide ( $\text{ZrO}_2$ ) and hafnium oxide ( $\text{HfO}_2$ ). This can be the case with spinels in which the oxides  $\text{MgO}$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  are not already a component of the ternary system or the spinel, particularly with a chromate spinel or an aluminate spinel. A zirconium oxide or hafnium oxide present in the spinel is partially or fully stabilized particularly with yttrium oxide ( $\text{Y}_2\text{O}_3$ ) or another rare earth oxide. A rare earth metal is hereby understood to mean, for short; one of the elements scandium, yttrium, lanthanum, as well as the lanthanides such as cerium and ytterbium. Furthermore, oxides of the actinides may also be added.

The bond coat has preferably an alloy that comprises at least one element of the spinel. Hence, through at least partial oxidation of the bond coat, an oxide is formed of this element that is also contained in the spinel, e.g., aluminum, chromium, cobalt or others to provide good adhesion of the spinel to the bond coat. The bond coat is preferably an alloy of the type  $\text{MCrAlY}$ , where  $\text{M}$  represents an element or several elements of the group comprising iron, cobalt or nickel,  $\text{Cr}$  represents chromium,  $\text{Al}$  aluminum, and  $\text{Y}$  yttrium or a reactive rare earth element. Furthermore, the bond coat can include, e.g., 1 to 15 wt-% rhenium. The chromium content preferably ranges from 3% to 50%, particularly from 12% to 25%, the aluminum content is preferably between 3% and 20%, particularly between 5% and 15%. The yttrium content is preferably between 0.01% and 0.3%.

The product is preferably a component of a thermal turbo machine, particularly a gas turbine. In particular, it is a turbine moving blade, a turbine stationary blade, or a heat shield of a combustion chamber. The metallic basic body preferably has a nickel-, cobalt- and/or chromium based superalloy. It is also possible to provide a furnace or similar component with a thermal barrier coating made of a spinel.

The advantage of the spinels is their high tolerance to impurities, e.g., due to the formation of simple or complex mixed crystals in the presence of iron, aluminum, nickel, chromium or other metals, a good characterization of the sintering behavior of the high-melting spinels, and an essentially cubic structure and therefore quasi isotropic thermal expansion. Spinels furthermore exhibit good chemical resistance, high thermal shock resistance and high strength. Even with a transition of a spinel from its normal form to the inverse form, or at least partially to the inverse form, there are no abrupt changes in the physical-chemical properties. The transition from normal to inverse spinel can thus be considered an order-disorder induced phase transition of the second order, which has no great influence on the properties of the thermal barrier coating.

Thermal barrier coatings with a spinel may be produced, for example, by simple plasma spraying. A thermal barrier coating with a corresponding porosity can be produced by atmospheric plasma spraying. Alternatively, the thermal barrier coating may be applied by means of vapor deposition, e.g., an electron beam PVD process, with an adjustable columnar structure.

Preferably, the thermal barrier coating is applied by atmospheric plasma spraying, particularly with a predefinable porosity. The metallic mixed oxide system may also be applied by means of a suitable vapor deposition process, a suitable PVD process (Physical Vapor Deposition), particularly a reactive PVD process. When the thermal barrier coating is applied by means of vapor deposition, e.g., an electron beam PVD process, a columnar structure can be achieved if required. In a reactive PVD process, a reaction, particularly a conversion, of the individual components of a ternary oxide or a pseudo ternary oxide takes place only during the coating operation, particularly directly upon striking the product. In non-reactive vapor deposition, the previously pre-reacted products, particularly the ternary oxides with a perovskite structure are evaporated and are then deposited from the vapor onto the product. The use of pre-reacted products is advantageous particularly if plasma spraying is used.

The production (synthesis) of the spinels, e.g.,  $\text{NiCr}_2\text{O}_4$ ,  $\text{NiAl}_2\text{O}_4$  and  $\text{MgCr}_2\text{O}_4$  can be carried out phase-shift-free in the "mixed oxide process." In this case, the starting powders used are the associated binary oxides, e.g.,  $\text{Cr}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . These powders can be homogenized under isopropanol, cold isostatically pressed, particularly at a pressure of 625 mPa, and subsequently tempered for 50 hours at  $1500^\circ\text{C}$  in air at a heat rate of 5 K/min.